The NPL Measurements Contribution to the Certification of Pyroceram 9606 as a Reference Material for Thermal Properties

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ABSTRACT

As part of a European characterisation and measurement programme to certify the thermal conductivity and diffusivity of Pyroceram 9606 as a reference material for temperatures up to 1000 °C several European organisations carried out investigations of those properties for which they had appropriate capabilities. The present paper contains details of one programme of such measurements involving different methods.

Thermal conductivity was measured by absolute methods including the standard guarded hot plate and transient line source techniques, the latter being used in both the resistive and parallel wire modes. Particular attention is drawn to the modifications and additional requirements for obtaining adequate specimen forms and reliable thermal measurements for this relatively high thermal conductivity material. The thermal diffusivity was measured using the laser flash method on specimens with different surface coatings. The specific heat capacity was obtained from results of differential scanning calorimetry. In all cases measurements were undertaken on multiple specimens from the same material batch and included repeats.

The results are presented and discussed, particularly with respect both to the verification of the claimed measurement uncertainties and to the final certified values. All individual property values were within the final uncertainties established for the certified values. Furthermore thermal conductivity values calculated from thermal diffusivity and specific heat capacity measurements were also within the measurement uncertainties.

Keywords. Certified reference material, emissivity, specific heat capacity, thermal conductivity, thermal diffusivity, thermal expansion,

1 INTRODUCTION

Pyroceram 9606 has been used by many workers for over 30 years as an uncertified reference material for thermal conductivity based primarily on its known reproducibility and stability and property values recommended by Powell and colleagues [1] as a result of a critical evaluation of published data. Very recently as a result of a comprehensive two part characterisation and certification programme, funded by the European Commission, and involving eleven organisations from six countries, representative certified values for both thermal conductivity and thermal diffusivity have been published [2 and 3]. The material is now available as a Certified Reference Material from Institute of Reference Materials and Measuremetns (IRMM) in Geel, Belgium (www.irmm.jrc.be).

For the certification requirements, it was necessary that measurements of each individual transport property would have to be undertaken by at least two different absolute methods involving six organisations in total in order for the exercise to be considered statistically valid. In addition it was also decided that one or more laboratories would carry out supplementary measurements of some directly related and relevant properties, including specific heat capacity, linear thermal expansion and radiation transmission properties. These would not only confirm that thermal transmission in this material was predominantly by conduction processes but also enable thermal conductivity to be derived from the directly measured thermal diffusivity.

The above overviews of the total characterisation and certification programmes contain detailed summaries of all the results and their subsequent analysis. However, primarily because of space limitations, they do not include much of the necessary and vital information relating to a particular method or methods used by the individual organisations in order to obtain reliable results. Furthermore it was decided by the participants that it would be more appropriate for the organisations concerned to provide this information separately.

The current paper thus contains specific information relating to the methods used by the National Physical Laboratory especially for the determination of thermal conductivity and thermal diffusivity. The former property was measured by both the standard guarded hot plate [4] and the hot-wire [5] methods. The latter was used in both the resistive and parallel wire forms since these modes were considered sufficiently different to be classed as individual methods. The thermal diffusivity was measured by the laser flash method [6] using a similar technique to that of several other partners. Specific heat capacity was also measured on one specimen using differential scanning calorimetry in a similar manner to all other partners. The parallel hot-wire method can also be used to measure thermal diffusivity and specific heat capacity at the same time as the thermal conductivity- albeit with a higher measurement uncertainty than for thermal conductivity. The results for these properties were not included in the certification but are included here to illustrate the viability of the methods and the potential level of measurement uncertainty attainable. Finally thermal expansion and thermal transmissivity results were also included. The results of the latter are presented in an earlier paper on the Certification of Pyroceram 9606 [3] and were made mainly to verify that the material is essentially opaque and that heat transmission is predominantly by conduction.

2 MEASUREMENTS

2.1 THERMAL CONDUCTIVITY

A basic issue to be faced with Pyroceram 9606 is the limited availability of the material in suitably large forms for absolute steady state measurements. The hot plate method usually requires a large specimen of such a thickness that the overall thermal resistance is within well defined limits. Ideally the hot-wire method requires a pair of specimens in the form of brick sized pieces. Hence, for the present study the final specimen sizes were a compromise based on the fact that the maximum thicknesses available were of the order of 40 to 50 mm. This limitation meant that greater care than normal was taken in instrumenting and assembling the specimens for measurement.

2.1.1 Guarded hot-plate (ghp)

Measurements were undertaken over the temperature range 300 to 800°C using the standard NPL high temperature guarded hot-plate [7] in the double-sided mode having a measurement uncertainty of ±5% over the temperature range. However, because the thermal conductivity of Pyroceram 9606 (~4 W/m·K at 20°C) is much higher than the materials for which it was originally designed, the apparatus had to be temporarily modified and three basic issues had to be dealt with as follows:

1) *Extraction of the extra heat conducted through the specimen.* The thermal resistance between the heated cold plates and the chilled plates of the apparatus was decreased so that as low a minimum specimen temperature as possible could be achieved without reducing the temperature gradient across the specimen to an unacceptably low level. To decrease thermal resistance some of the calcium silicate insulation between the heated cold plate and chilled plates, used as a heat sink, was replaced with steel disks.

2) *The specimens could not be made large enough to cover the whole area of the heater and cold plates.* Each specimen in the pair (HT58A and HT58B) had to be manufactured as two semi-cylinders of the same size because of the limited size of the available blocks from which they could be machined. When put together the diameter of the specimens was such that they covered the central part of the main heater plate i.e. up to the inner edge of the guard/centre gap rather than the midpoint of the gap.

3) *Thermal contact resistance between the heater plates and specimen.* Grooves were cut into the specimen faces to accommodate the thermocouples. Details of the mass and dimensions of the specimens and grooves prior to testing are listed in **Table 1**. Metal-sheathed 2 mm diameter Type N thermocouples were cemented into the grooves, as shown in **Figure 1**, using Autostic® high temperature cement. The effective specimen thickness at room temperature for calculating thermal conductivity was taken as the mean distance between the junctions of the thermocouples on adjacent faces.
To complete the specimen assembly described above two annular shapes were machined from low-density pre-baked calcium silicate to fill in the spaces above and below the lateral guard area of the main heater plate. These all had the same outer diameter as the main heater plate whilst their inner diameters and thicknesses were made equal to the specimen diameter and thickness respectively.

Table 1. Specimen and groove details prior to test for each specimen and the mean values

Sample dimensions (mean)	HT58A	HT58B	Mean
Diameter / mm	148.15	148.39	148.27
Thickness / mm	40.28	40.28	40.28
Total Groove Volume / mm³	2632	2760	2696
Mass / g	1790.9	1795.8	1793.4
Density / (kg/m^3)	2589	2588	2588

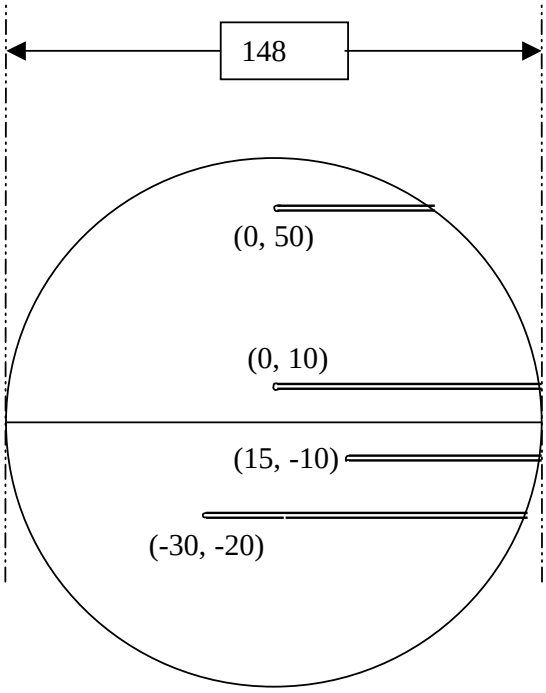

Figure 1. Schematic of the instrumented specimen. The (x-y) co-ordinates indicate the position of the junction on one specimen face relative to the centre of the specimen. All dimensions in millimetres.

Grooves were also cut into the calcium silicate surfaces in the guard area to accommodate the specimen thermocouples. To maximise uniformity of thermal contact resistance between the plates of the apparatus and the specimens and calcium silicate annuli 2 mm thick ceramic fibre blanket insulation was placed between the specimens and the heater plates. The entire assembly between the main heater plate and heated cold plate is illustrated in **Figure 2.**

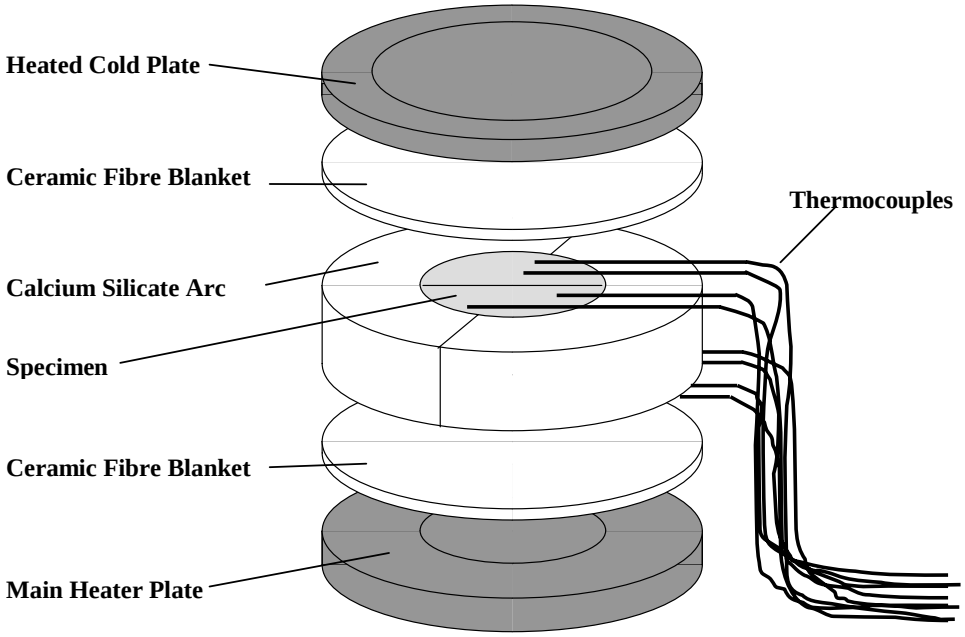

Figure 2. Layout of the upper specimen stack in the guarded hot plate.

To ensure uniform heat flux through the specimens correct alignment of the specimens with the metering area of the main heater plate was very important. During assembly the ceramic fibre insulation obscured the view of the edge of the metering area, therefore a special procedure was developed for aligning the specimens. Firstly, the lower specimen was centralised on the lower heated cold plate by measuring its distance from the plate edge at several places. Then the calcium silicate annulus was put into place, with care being taken not to dislodge the specimen. Next, the main heater plate was suspended just above the specimen using wires attached to the upper chilled plate. This was lowered until it just touched the blanket above the specimen and gently shifted around until its edges were found, by means of a square, to be in perfect alignment with the edges of the lower heated cold plate. In theory, because the plates were well made to tight dimensional tolerances then the edge of the metering area would be aligned with the specimen. A similar procedure was followed for the assembly of the upper specimen.

Some preliminary tests were carried out to check the performance of the assembly. It was found that the lowest mean specimen temperature that could be obtained with a temperature drop, ΔT, across the specimen of 30 °C was 400 °C, though 300 °C could be obtained with a ΔT of 20 °C. As a result one measurement was done at 300 °C with a ΔT of 20 °C followed by measurements from 400 °C to 800 °C in 100 degree steps, all with a ΔT of 30 °C. Each temperature controller had to be re-tuned individually and a small modification made to the power correction routine in the automation software, which was found to be adjusting the metering area power during steady state to anomalous levels.

On completion of each experiment the results were corrected for thermal expansion of both the specimen thickness and area using expansion data obtained from the characterisation part of the project. Normally the software uses the distance between

the centre of the plate and the mid-point of the guard/centre gap as the radius of the metering area used in the calculation. However, for these tests the area used was the actual specimen face area, which covered the metering plate area exactly and therefore a small correction was also made for this difference.

The entire experiment was repeated from start to finish to check for repeatability. This included the removal and re-cementing of the thermocouples. Measurements of the dimensions and masses were taken on final dismantling of the specimen in order to verify that the density had not changed during the temperature cycling.

2.1.2 Hot-wire method

The thermal conductivity was measured using a commercial high temperature transient hot wire apparatus in both resistive and parallel wire modes between room temperature and 1000 °C; the measurement uncertainty is ±5% over the temperature range. Tests were carried out on two specimen pairs having dimensions as required by ISO8894-2. The specimen pair named HW53 was machined from blocks 3 and 4 of the batch of Pyroceram 9606 and the pair HW55 from blocks10 and 11. The second pair was measured approximately one year later than the first as it had been measured in the first round of measurements by one of the other partners.

The dimensions and masses of both pairs in the as received state are listed in **Table 2**. It should be noted that the density of specimen pair HW55 is about 1% lower than the other pair because it had already been tested twice at high temperatures and had experienced the small but significant change in density as indicated by the characterisation testing of the material. Each pair had the standard pattern of grooves cut into them to accommodate heater and thermocouple wires, i.e. grooves to accommodate the heater and main thermocouple wires in the lower specimen and a groove to accommodate the reference thermocouple in the upper specimen as shown in **Figure 3**. For HW53 the grooves were rectangular and 0.8 mm wide by 0.8 mm deep. HW55 was received by NPL with heater and main thermocouple grooves cut by the previous partner but these were too wide and deep for the NPL apparatus. A new set of grooves was therefore cut in the opposite face of the relevant specimen. These were circular rather than rectangular, with a cross sectional radius of 0.5 mm. All thermocouples used were Type S with diameters of 0.35 mm and a pure platinum wire of diameter 0.35 mm and length 200 mm was used as the heater.

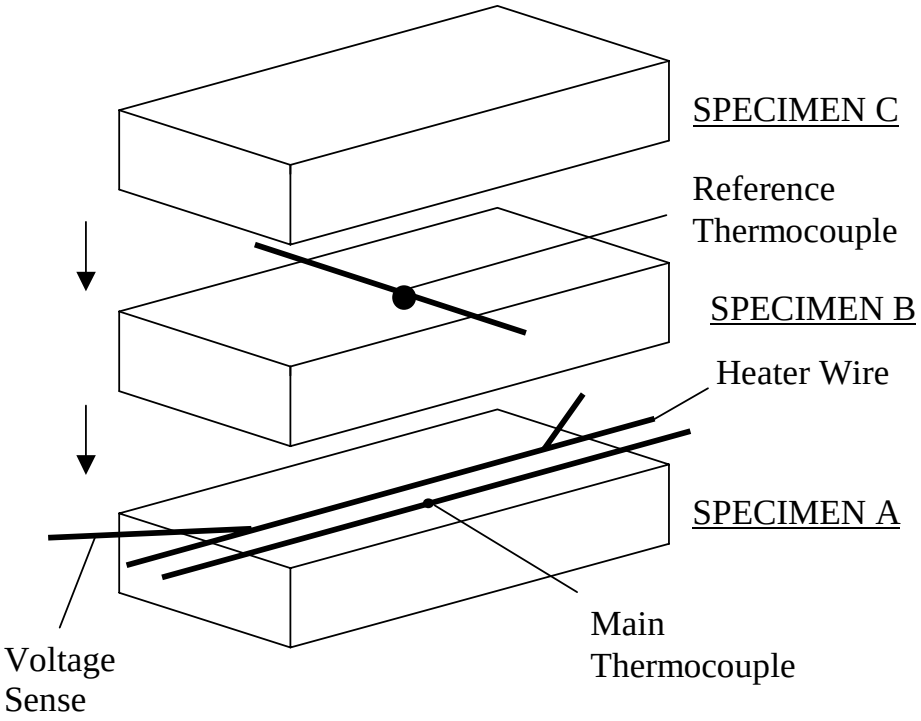

Figure 3. Layout of heater and thermocouple wire grooves on a hot-wire specimen.

Table 2. Mass and dimensions of specimens as received.

	HW 53A	**HW 53B**	**HW55A**	**HW55B**
Length / mm	230.29	231.15	232.64	231.307
Width / mm	91.97	91.85	90.963	90.667
Height / mm	48.92	51.05	50.620	50.433
Mass / g	2692.9	2814.5	2738.4	2724.7
Groove Volume / mm^3	333.17	58.78	1295.3	-
Chip Volume / mm^3	-	-	-	150
Density / Kg/m^3	2599.9	2596.9	2559.5	2576.5

The volume of material removed to make the grooves was calculated in order to make as realistic a measurement of specimen density as possible in each case. The volume of material lost through chipping on two of the specimens was also estimated. Preliminary measurements were performed on the first two specimen pairs to establish that reasonable results could be obtained for either pair and to determine the

best experimental parameters. Then each specimen pair was measured twice in both modes. The specimens were removed and re-installed between the first and second runs to check for repeatability but not between measurements done in different modes, i.e. each specimen was tested in resistive and parallel mode before removal and re-setting.

The thermal conductivity of HW53 was measured during the heating cycle only, whilst HW55 was measured in both the heating and cooling cycles to check for hysteresis. Three individual measurements were done at each temperature in each case.

Although the specimens came in pairs three specimens are normally required for a test, with the third specimen placed on top. Tests were initially carried out using an alumina specimen on top of the upper Pyroceram specimen for HW53 and HW55. However, this produced anomalous results, so for each pair tested one specimen from another pair was used as the third specimen.

For each test the results were manually re-analysed to select the most appropriate portion of the heating curves for resistive mode and of the thermal conductivity versus time curves for parallel mode. Any anomalous results within each group of three measurements at a given temperature were rejected and the remainder averaged.

2.2 THERMAL DIFFUSIVITY

NPL was one of the organisations undertaking laser flash thermal diffusivity measurements for the characterisation programme. The methodology is well known and the basis of the current NPL standard apparatus is provided in **Table 3**. Each participant used four specimens, two of which had been coated with tungsten by KE, one of the other partners, and two coated with the normal coating used by the individual participant. At NPL this is achieved by spraying with a colloidal graphite coating to a thickness of approximately 10 μm. Measurements were taken at regular 100°C temperature intervals above 100°C and data provided on pro-forma sheets for subsequent evaluation as described in the certification programme [3].

For the purposes of the certification each participant had to provide an uncertainty budget for its measurement procedure. For the present system this had been developed based on the following known major sources of uncertainty.

2.2.1 Thickness measurement

The measurement uncertainty is due to the resolution of the micrometer used and its calibration uncertainty. Those relative uncertainties are calculated and based on a 1 mm thick specimen. Since the thermal diffusivity to be measured is dependent on the square of specimen thickness, a factor of 2 is used in the uncertainty calculation for the thickness measurement.

Table 3. Specifications of NPL laser flash thermal diffusivity apparatus.

Measurement method	Laser flash technique [6]; Pulsed laser beam (Nd:Glass, 1064 nm wavelength); heating of the specimen on one face with pulsed laser beam; measurement of temperature rise of the other face (non-heated), by using an InSb infrared detector.
Manufacturer and type of instrument	Self constructed, in 1982, continually upgraded based on improvements in instrumentation and technology. These include linearisation of the detector output, averaging of five individual measurements and an improved high temperature furnace. Originally 50°C to 1600°C now 20°C to 1600°C.
Sensor used to detect sample temperature variations	Infrared detector (InSb detector between room temperature and 1600 °C)
Specimen dimensions	Diameter x thickness: 12 mm x 1-4 mm
Specimen coating; thickness	Colloidal graphite spray; 10-20 µm
Ambient atmosphere, pressure	Vacuum, 1 x 10^{-5} mbar
Evaluation procedure including heat losses	Originally Cowan $10t_{0.5}$ [7] for correcting heat loss effect; Taylor and Clark's method for correcting pulse duration effect [8]. For noisy signals a curve fitting method is used that is based on a least sqares analysis that uses all or most of the experimental curve (10^4 data points). New software developed based on Cape and Lehmann [9] and Cezarliyan et al [10].
Estimation of heat losses	Calculation according to definitions of Cowan [7].
Estimation of specimen temperature	By using a type-R thermocouple located in the vicinity of the specimen back face, with regular temperature calibration using dummy specimen.
Verification of traceability	Annual internal calibration of micrometer and data acquisition system. Annual thermal diffusivity measurement on a POCO-graphite (AXM-5Q1) reference material. Participation in two international intercomparisons [11 and 12]

The thermal expansion of the specimen in the thermal diffusivity calculation is set to null, and the effect of expansion can be compensated for in terms of the change in specimen thickness, provided its thermal expansion is known. An uncertainty of 1% in specimen thickness due to thermal expansion will result in an uncertainty in diffusivity of 2%. In the uncertainty budget, the thermal expansion component of uncertainty only accounts for sample temperature uncertainty, i.e. a 10 K temperature uncertainty with a 10^{-5} K^{-1} thermal expansion coefficient leading to a 0.01% uncertainty in sample thickness measurement.

2.2.2 Oscilloscope time base and signal measurement

These uncertainties are due to the resolutions of the oscilloscope and its calibration uncertainties. As the thermal diffusivity to be measured is inversely proportional to the half rise time, $t_{½}$ measured during an experiment, a factor of 1 is used in the uncertainty calculation for the time measurement. Since the vertical signal is measured in a relative way, its uncertainty has to be converted to an equivalent uncertainty in the time measurement with use of the conversion factor c_V, calculated later.

2.2.3 Non-uniformity of laser

It is difficult to estimate accurately the uncertainty in the thermal diffusivity measurement due to the effect of the non-uniformity of the laser, because the uniformity of a laser may change from shot to shot, and it is also dependent on the energy level of the laser beam. A 3% uncertainty due to the effect of laser non-

uniformity is assumed in this uncertainty budget. This is based on recent work of Sheindlin et al [11] who have investigated this uncertainty experimentally by mapping the thermal diffusivity across sample surfaces with different laser beam profiles. It was found that the radial uncertainty was within 3%, while the signal levels changed significantly for spot to spot measurements.

2.2.4 Temperature measurement

As thermal diffusivity is usually not a strong function of temperature, there is no need to know the specimen temperature very accurately. Due to the cylindrically symmetric structure of the tantalum furnace and the central location of specimen, the temperature gradients in depth and in plane have been found to be small. Moreover, since the temperature rise caused by the laser heating is transient and relatively small, small temperature gradients inside the specimen will not affect the temperature rise significantly according to linear thermal diffusion theory. Nevertheless, a 10 K uncertainty of temperature due to temperature gradients and the temperature measurement by the thermocouple has been included in this uncertainty budget. This uncertainty is calculated based on the uncertainty in thermal expansion for a typical expansion coefficient of 10^{-5} K^{-1}.

2.2.5 Thermal radiation and IR detector non-linearity

The non-linearity in thermal radiation is because the thermal radiation from a grey body is proportional to the fourth power of its absolute temperature. The calculation in this budget is based on the case of a typical temperature rise of 5 K at room temperature 300 K (the poorest case). The non-linearity effect of the IR detector is assumed to be negligibly small because the temperature rises inside a specimen only have a small effect on the radiation received by the detector.

2.2.6 Other uncertainties

There are various other sources of uncertainty such as electronic noise, baseline drift, etc. These usually have a very small effect on the determination of thermal diffusivity and hence are not evaluated individually. However, a repeatability statement can be determined from the annual calibration of the system using an AXM-5Q1 Pocographite reference specimen and this is illustrated in **Figure 4.** The data follows a normal distribution curve, and 95% of the data falls within 3.7% of the centre line.

Based on the above factors an uncertainty budget for the method is provided in **Table 4**. Overall the uncertainty is ±4% at the 95% confidence limit for well-prepared specimens and the reproducibility for the apparatus is better than 1.5%. The uncertainty budget shown in the Table was carried out assuming a 1 mm thick specimen having an expansion uncertainty of 10^{-4} and a temperature rise of 5 K at 300 K. It also assumes that the non-uniformity of the laser beam causes 1.5 % uncertainty in the thermal diffusivity measurement, the variation (standard deviation) of five specimen thickness measurements is 0.5 % and the repeatability of five thermal diffusivity measurements is 1 %. Therefore this uncertainty budget can be considered to be that for a worst-case test situation.

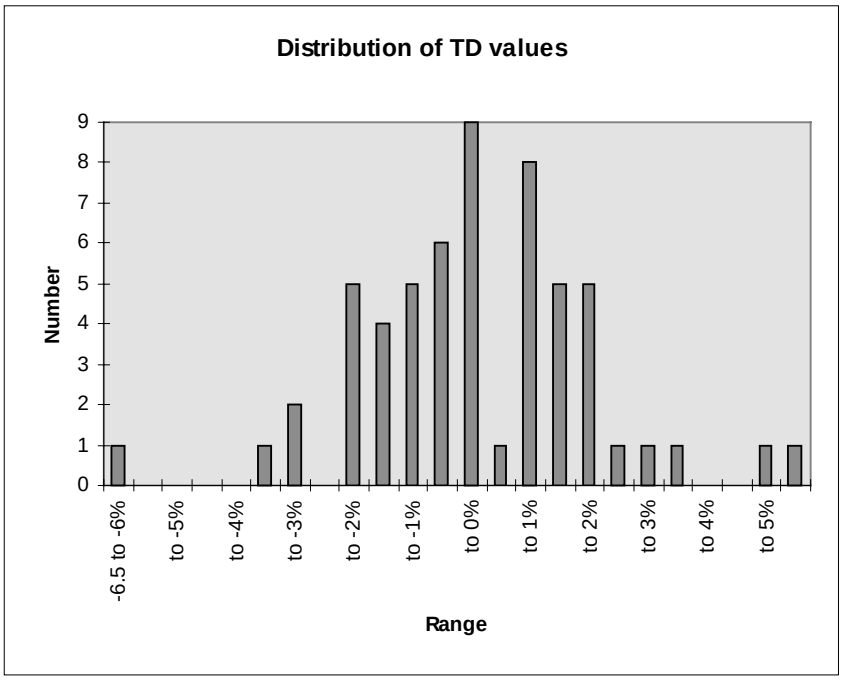

Figure 4. Distribution of NPL measured thermal diffusivity values of POCOGraphite specimen obtained over 12 years. (The data follow a normal distribution curve and 95% of the values fall within 3.7% of the mean value.)

3 RESULTS AND DISCUSSION

3.1 THERMAL CONDUCTIVITY

The experimental results are presented in **Table 5** and **Table 6**, for measurements by the guarded hot plate and the hot-wire methods respectively. The tables also contain values at regular 100°C temperature intervals calculated from curve fitting the experimental data for each method. For this material the thermal conductivity will vary linearly with inverse absolute temperature since the heat transmission mechanism is primarily by phonons as radiation has been shown by the results of transmission tests to be negligible.

The results for the individual methods, shown graphically in **Figure 5**, indicate that the two hot-wire methods produce broadly equivalent results particularly at the higher temperatures with possibly greater uncertainty below approximately 200°C. Over the common temperature range 300°C to 800°C it can be seen that there is very good agreement between the results, well within the uncertainties of each method, such that the three sets can be combined to produce a common curve. **Figure 5** also includes the Certified values obtained for the overall Certification and shows that the NPL values are in good agreement over the whole temperature range. The maximum difference rises to about 3% at the highest temperature. The final values from the NPL measurements can be represented by the following linear function of the inverse absolute temperature (T in K).

$$\lambda = 483.01/T + 2.4483 \text{ W/m.K}$$

Table 4. Uncertainty budget for measurements using the NPL laser flash apparatus. Assumes a 1 mm thick specimen, an expansion uncertainty of 10^{-4} and a temperature rise of 5 K at room temperature.

Parameter	Source of uncertainty	Value ±%	Probability distribution	Divisor	c_i	Diffussivity Uncertainty ±%	V_i or V_{eff}
Thickness	Flatness	0.025	Rectangular	$\sqrt{3}$	2	0.0289	∞
	Parallelism	0.25	Rectangular	$\sqrt{3}$	2	0.2887	∞
	Zero reading	0.13	Rectangular	$\sqrt{3}$	2	0.1444	∞
	Range of error of traverse of Micrometer screw	0.25	Normal	2	2	0.25	∞
	Error in alignment	0.06	Normal	2	2	0.06	∞
	Uncertainty of calibration measurement	0.51	Normal	2	2	0.51	∞
	Variation in sample thickness	0.5	Normal	1	2	1	4
Combined uncertainty			Normal			1.431	8
oscilloscope	Timebase calibration	0.25	Normal	2	1	0.125	∞
	Vertical calibration	1.0	Normal	2	c_V	0.7684	∞
	Timebase resolution	0.1	Rectangular	$\sqrt{3}$	1	0.0577	∞
	Vertical resolution	0.4	Rectangular	$\sqrt{3}$	c_V	0.3549	∞
Combined uncertainty			Normal			0.8575	∞
Laser	Non-uniformity	3	Normal	2	1	1.5	∞
Temperature	Thermal expansion	0.01	Normal	2	2	0.01	∞
Non-linearity	Thermal radiation	1.239	Rectangular	$\sqrt{3}$	c_V	1.0994	∞
Measurement repeatability		1	Normal	1	1	1	4
Total combined uncertainty			Normal			2.69	>67
Expanded uncertainty			Normal (k=2)			5.38	>67

Table 5. Guarded hot plate results for specimens prepared from block 17 of the Pyroceram batch.

Initial test		Repeat		Fitted data	
Temp /°C	Lambda /(W/m.K)	Temp /°C	Lambda /(W/m.K)	Temp /°C	Lambda /(W/m.K)
300.1	3.31	301.2	3.26	300	3.27
402.5	3.16	400.3	3.13	400	3.16
500.9	3.07	500.4	3.07	500	3.08
600.4	3.02	600.3	3.00	600	3.02
701.2	2.95	701.3	2.95	700	2.96
802.3	2.94	801.6	2.95	800	2.92

Table 6. Hot-wire results for specimens cut from blocks 3, 4 10 and 11 of the Pyroceram batch.

Nominal Temp /°C	Resistive Thermal conductivity / (W/m.K)				Parallel Thermal conductivity / (W/m.K)				Mean Lambda /(W/m.K)
	Spec 1	Repeat	Spec 2	Repeat	Spec 1	Repeat	Spec 2	Repeat	
100	3.65	3.68	3.75	3.74	4.03	3.59	4.23	4.35	3.88
200	3.51	3.39	3.53	3.56	3.56	3.38	3.64	3.72	3.54
300	3.48	3.43	3.25	3.42	3.36	3.31	3.45	3.49	3.40
400	3.24	3.20	3.21	3.27	3.32	3.24	3.26	3.25	3.25
500	3.15	3.03	3.11	3.16	3.29	3.11	3.16	3.24	3.16
600	3.04	3.14	2.98	2.99	3.03	3.01	2.99	3.04	3.03
700	2.94	2.90	2.84	2.88	2.98	2.92	2.86	2.95	2.91
800	2.87	2.96	2.76	2.86	2.96	2.72	2.75	2.75	2.83
900	2.91	2.83	2.79	2.66	2.82	2.78	2.74	2.76	2.79
1000	2.68	2.72	2.60		2.94	2.88	2.69		2.75

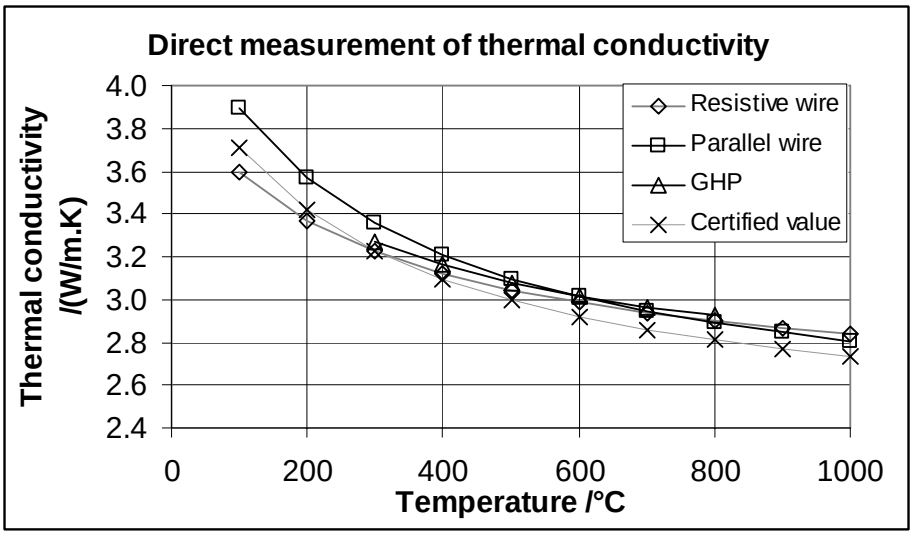

Figure 5. Thermal conductivity of Pyroceram 9606 by three methods and compared with the Certified value.

3.2 THERMAL DIFFUSIVITY

3.2.1 Laser flash measurements

From the results of the measurements on the four specimens the reciprocal of the thermal diffusivity was fitted to a fourth order polynomial function of temperature for each specimen and then values of thermal diffusivity were calculated at 100°C intervals as shown in **Table 7**. They indicate that the two different coatings used for the measurements have no significant effect on the result, that the material is homogeneous and that the apparatus provides very reliable and reproducible results well within the claimed uncertainty for the equipment. The mean of the four measured

thermal diffusivity values, a, can be represented by the following equation, where T is the specimen temperature in °C, to better than 1.4%.

$a = 1/(-2.9037x10^{-13}.T^4 + 9.4539x10^{-10}.T^3 - 1.2700x10^{-6}.T^2 + 1.2710x10^{-3}.T + 0.49584)$

The results range from approximately 1 % higher than the Certified values at the upper and lower ends of the temperature range and from 1 to 3.5% below the Certified values between 100°C and 600°C.

Table 7. Summary of laser flash thermal diffusivity results on four specimens

Temp °C	Thermal diffusivity/ $(m^2/s)*10^{-6}$					Deviation %	
Specimen	1.42(W)	1.43(W)	1.44(C)	1.45(C)	**Mean values**	Max	Standard
25	1.915	1.938	1.909	1.912	**1.918**	1.53	0.60
50		1.772			**1.772**	0.00	0.00
100	1.652	1.599	1.686	1.638	**1.644**	5.29	1.89
200	1.396	1.406	1.434	1.401	**1.409**	2.72	1.05
300	1.269	1.277	1.294	1.275	**1.278**	1.91	0.71
400	1.163	1.165	1.193	1.171	**1.173**	2.55	1.03
500	1.079	1.087	1.103	1.089	**1.090**	2.22	0.80
600	1.014	1.044	1.048	1.035	**1.035**	3.21	1.24
700	0.967	0.980	0.989	0.982	**0.980**	2.22	0.81
800	0.933	0.943	0.943	0.946	**0.941**	1.32	0.51
900	0.890	0.912			**0.901**	2.42	1.21
1000	0.849	0.861	0.884	0.878	**0.868**	4.08	1.61

3.2.2 Hot-wire measurements

As indicated earlier the parallel version of the hot-wire method can also be used to determine both specific heat capacity and thermal diffusivity. Due to the fact that the uncertainty in the results is larger than that for the thermal conductivity they were not used in the final certification of Pyroceram 9606. However they are being included in this paper to indicate the magnitude of the measurement uncertainty and hence the degree to which the results using this method can be accepted.

The results are summarised in **Table 8** and **Table 9** for thermal diffusivity and specific heat capacity respectively. Measurements of the property by laser flash and differential scanning are also included for comparison in the respective tables. Overall the results indicate that there is very good agreement between results obtained by the hot wire technique and those measured by the flash method and DSC respectively. This is especially true for temperatures in excess of 200°C and also the reproducibility is much better at higher temperatures for both properties.

3.2.3 Derivation of thermal conductivity

Since the material has been shown to be homogeneous and heat transmission is by conduction the present results for the individual properties can be used to derive thermal conductivity. Measurements of linear thermal expansion were also undertaken and as a result the density calculated at each temperature. Using the experimental values for thermal diffusivity, specific heat capacity and density the thermal conductivity has been derived from the relationship $\lambda = a.\rho.C_p$

The results are summarised in **Table 10** which also contains the present mean thermal conductivity from guarded hot plate and hotwire measurements, the thermal conductivity certified in the EC project [3] and the NSRDS previously recommended thermal conductivity values [1].

Table 8. Summary of thermal diffusivity values obtained from hot-wire measurements.

Nominal Temp /°C	Thermal diffusivity (m^2/s)*10^{-6}					
	Specimen 1	Specimen 1 Repeat	Specimen 2	Specimen 2 Repeat	Hot wire Mean value	Laser flash Fitted
25.5	2.00	1.90			1.950	1.896
47.0			1.850	1.766	1.808	1.809
94.2	1.70	1.60	1.730	1.466	1.624	1.653
191.5	1.50	1.40	1.400	1.300	1.400	1.431
291.5	1.20	1.30	1.300	1.200	1.250	1.282
392.5	1.20	1.20	1.200	1.100	1.175	1.177
494.0	1.10	1.10	1.100	1.000	1.075	1.098
595.3	1.00	1.00	1.030	0.980	1.003	1.036
696.0	1.00	1.00	0.965	0.910	0.969	0.984
797.2	1.00	0.90	0.900	0.893	0.923	0.940
898.3	0.90	0.89	0.880		0.890	0.902
999.0	0.90	0.89	0.845		0.878	0.868

Table 9. Summary of specific heat capacity results from hot wire and differential scanning calorimetry.

Mean Temp /°C	Specific Heat / (J/kg.K)					
	Specimen 1	Specimen 1 Repeat	Specimen 2	Specimen 2 Repeat	Hot wire Mean value	NPL DSC values
25.5	790	767			779	819
47.0			954		954	850
94.2	875	856	952	958	910	909
191.5	952	952	1001	1005	978	999
291.5	1032	1022	1036	1039	1032	1060
392.5	1076	1072	1081	1079	1077	1100
494.0	1119	1099	1087	1095	1100	1129
595.3	1149	1145	1127	1133	1138	1151
696.0	1180	1165	1163	1171	1170	1172
797.2	1197	1176	1197	1179	1187	1191
898.3	1222	1207	1207	1208	1211	1207
999.0	1289	1249	1233		1257	1215

Table 10. Summary of thermal conductivity values including value calculated from thermal diffusivity measurements.

Temp °C	Density kg/m^3	Specific heat capacity J/kg.K	Thermal diffusivity m^2/s.10^{-6}	Thermal conductivity /(W/m.K) Calculated from diff.	Mean ghp and hot wire	Certified values	NSRDS values
25	2597	818	1.898	4.03	3.96	4.06	4.02
50	2595	854	1.797	3.98	3.85	3.93	3.90
100	2593	915	1.636	3.88	3.67	3.71	3.72
200	2588	1005	1.416	3.68	3.43	3.42	3.47
300	2585	1064	1.272	3.50	3.27	3.23	3.30
400	2582	1103	1.171	3.33	3.16	3.10	3.19
500	2578	1130	1.094	3.19	3.08	3.00	3.10
600	2575	1152	1.033	3.07	3.02	2.92	3.04
700	2572	1173	0.983	2.96	2.96	2.86	2.98
800	2569	1192	0.939	2.87	2.92	2.81	2.94
900	2566	1207	0.901	2.79	2.89	2.77	2.90
1000	2562	1215	0.868	2.70	2.86	2.74	2.88

4 CONCLUSIONS

Overall it can be seen that there is quite acceptable agreement between the calculated values and the measured values of Pyroceram 9606. The maximum divergence is some 7 to 8% in the temperature range 300°C to 400°C decreasing to less than 3% above and below this range. These results also confirm that heat transmission in Pyroceram 9606 is by conduction processes as discussed in the certification paper [3]. One final comment concerns the original thermal conductivity values recommended over thirty years ago. These were based on much less information and mainly on thermal diffusivity measurements. It is gratifying to discover that they differ from the present Certified values by less than 5% over the complete temperature range. Thus they are within the overall uncertainty limits of the present Certified values, which unlike previous similar intercomparisons include the uncertainty limits of each apparatus involved.

5 SUMMARY

The present paper describes in detail measurements of thermal conductivity and thermal diffusivity of a batch of Pyroceram 9606 undertaken by the National Physical Laboratory as part of a larger programme of work in order to provide Certified values of these thermal properties over the temperature range 25°C to 1000°C. For both properties the result obtained by the various methods involved were within the overall uncertainty levels of the Certified values. Additional properties were measured in order to derive thermal conductivity from the thermal diffusivity. There was good agreement between measured and calculated values indicating that heat transmission in Pyroceram 9606 is by conduction processes only.

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